



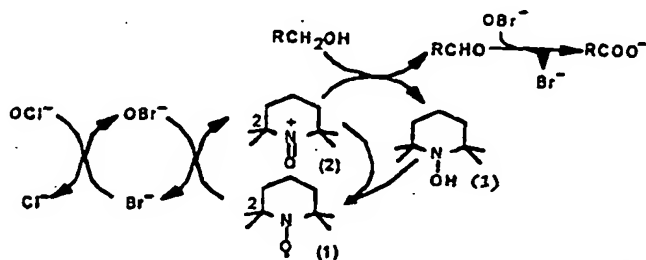
INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

(51) International Patent Classification ⁶ : C08B 15/04, C12S 3/00, D21C 9/10	A1	(11) International Publication Number: WO 99/23117 (43) International Publication Date: 14 May 1999 (14.05.99)
<p>(21) International Application Number: PCT/FI98/00861</p> <p>(22) International Filing Date: 4 November 1998 (04.11.98)</p> <p>(30) Priority Data: 974139 4 November 1997 (04.11.97) FI</p> <p>(71) Applicant (for all designated States except US): VALTION TEKNIILLINEN TUTKIMUSKESKUS [FI/FI]; Vuorimiehentie 5, FIN-02044 VTT (FI).</p> <p>(72) Inventors; and (75) Inventors/Applicants (for US only): VIIKARI, Liisa [FI/FI]; Lökkikuja 5 F, FIN-00200 Helsinki (FI). KRUUS, Kristiina [FI/FI]; Kaitalahdenranta 7, FIN-02260 Espoo (FI). BUCHERT, Johanna [FI/FI]; Alalinnake 5 A 9, FIN-02160 Espoo (FI).</p> <p>(74) Agents: LAINE, Seppo et al.; Seppo Laine Oy, Itämerenkatu 3 B, FIN-00180 Helsinki (FI).</p>	<p>(81) Designated States: AL, AM, AT, AU, AZ, BA, BB, BG, BR, BY, CA, CH, CN, CU, CZ, DE, DK, EE, ES, FI, GB, GE, GH, GM, HR, HU, ID, IL, IS, JP, KE, KG, KP, KR, KZ, LC, LK, LR, LS, LT, LU, LV, MD, MG, MK, MN, MW, MX, NO, NZ, PL, PT, RO, RU, SD, SE, SG, SI, SK, SL, TJ, TM, TR, TT, UA, UG, US, UZ, VN, YU, ZW, ARIPO patent (GH, GM, KE, LS, MW, SD, SZ, UG, ZW), Eurasian patent (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM), European patent (AT, BE, CH, CY, DE, DK, ES, FI, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE), OAPI patent (BF, BJ, CF, CG, CI, CM, GA, GN, GW, ML, MR, NE, SN, TD, TG).</p> <p>Published With international search report.</p>	

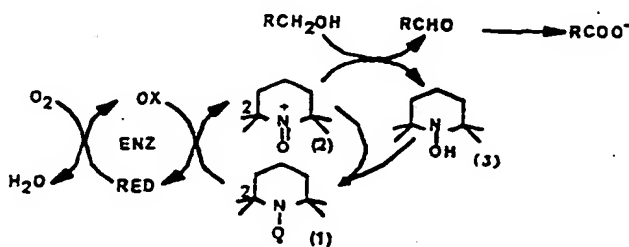
(54) Title: METHOD FOR MODIFICATION OF CELLULOSE

(57) Abstract

A method for preparing oxidized cellulose, which comprises bringing a cellulose-containing material into contact with a reactant, such as 2,2,6,6-tetramethylpiperidine-1-oxyl, producing an oxoammonium ion in the presence of an oxidizing agent. According to the invention, laccase is used as an oxidation agent. The invention provides selective oxidation, which gives rise to the formation of carboxylic and carbonyl groups at desired ratios in the cellulose. By using laccase it is possible to avoid the environmentally harmful halide-containing materials commonly used as oxidants.



A



B

FOR THE PURPOSES OF INFORMATION ONLY

Codes used to identify States party to the PCT on the front pages of pamphlets publishing international applications under the PCT.

AL	Albania	ES	Spain	LS	Lesotho	SI	Slovenia
AM	Armenia	FI	Finland	LT	Lithuania	SK	Slovakia
AT	Austria	FR	France	LU	Luxembourg	SN	Senegal
AU	Australia	GA	Gabon	LV	Latvia	SZ	Swaziland
AZ	Azerbaijan	GB	United Kingdom	MC	Monaco	TD	Chad
BA	Bosnia and Herzegovina	GE	Georgia	MD	Republic of Moldova	TG	Togo
BB	Barbados	GH	Ghana	MG	Madagascar	TJ	Tajikistan
BE	Belgium	GN	Guinea	MK	The former Yugoslav Republic of Macedonia	TM	Turkmenistan
BF	Burkina Faso	GR	Greece	ML	Mali	TR	Turkey
BG	Bulgaria	HU	Hungary	MN	Mongolia	TT	Trinidad and Tobago
BJ	Benin	IE	Ireland	MR	Mauritania	UA	Ukraine
BR	Brazil	IL	Israel	MW	Malawi	UG	Uganda
BY	Belarus	IS	Iceland	MX	Mexico	US	United States of America
CA	Canada	IT	Italy	NE	Niger	UZ	Uzbekistan
CF	Central African Republic	JP	Japan	NL	Netherlands	VN	Viet Nam
CG	Congo	KE	Kenya	NO	Norway	YU	Yugoslavia
CH	Switzerland	KG	Kyrgyzstan	NZ	New Zealand	ZW	Zimbabwe
CI	Côte d'Ivoire	KP	Democratic People's Republic of Korea	PL	Poland		
CM	Cameroon	KR	Republic of Korea	PT	Portugal		
CN	China	KZ	Kazakstan	RO	Romania		
CU	Cuba	LC	Saint Lucia	RU	Russian Federation		
CZ	Czech Republic	LI	Liechtenstein	SD	Sudan		
DE	Germany	LK	Sri Lanka	SE	Sweden		
DK	Denmark	LR	Liberia	SG	Singapore		
EE	Estonia						

Method for modification of cellulose

The present invention concerns a method according to the preamble of claim 1 for oxidizing cellulose.

According to the present method a cellulose-containing substrate is brought into contact with a reagent producing an oxoammonium ion in the presence of an oxidation agent. The reaction is preferably carried out in a liquid medium and the reaction product is separated from the medium after the reaction.

Pulp fibres contain cellulose as the major carbohydrate. By converting the primary alcohol groups of cellulose into carboxylic or aldehyde groups, the properties of cellulose can be modified. Thus, to mention an example, new carboxylic groups can be introduced into cellulose or a cellulose-based material by oxidation. Such carboxylic groups will affect the properties of cellulosic pulps; by increasing the carboxylic group content, the swelling and as a result the fibre flexibility can be increased. On an average, kraft pulps contain 30 to 150 mmol carboxylic groups/kg (3).

Carboxylic groups can be also generated onto different cellulose textile fibres, e.g. cotton and linen, in order to obtain novel properties for the end-product. For instance, the increase in carboxylic group content in cotton or linen will increase the water absorbency and subsequently affect fabric properties. Furthermore, by increasing the carboxylic group content in recycled fibres or in mechanical fibres the technical properties can be up-graded.

Nitrogen oxides have been used in chemical oxidation of carbohydrates (4). The disadvantage of oxidation with nitrogen oxides is that the method is not selective to primary alcohol groups. Also the secondary OH-groups are oxidized, which will cause depolymerization.

Semmelhack et al. (1983) showed that primary alcohol groups can be selectively oxidised

by a stable organic nitroxyl radical TEMPO. The actual oxidant is the oxoammonium ion, which can be obtained from TEMPO by chemical oxidation. Several oxidants e.g. hypohalites are able to oxidise TEMPO to oxoammonium ion. The oxidation of various natural occurring polysaccharides is discussed by Chang and Robyt (2).

To complete the survey it should be mentioned that Krishna et al (8) have studied the mechanism of superoxide dismutation by various 5- and 6-membered nitroxides. The superoxide was enzymatically generated.

The present invention is based on the idea that TEMPO can be enzymatically oxidized with, e.g. phenoloxidases such as laccases, to the oxoammonium ion. Therefore, laccases can be used to replace chemical oxidants which may be hazardous or even toxic. The present invention thus provides for oxidation of carbohydrates in cellulosic fibres by enzymatically oxidizing TEMPO.

More specifically, the present invention is mainly characterized by what is stated in the characterizing part of claim 1.

Considerable advantages are obtained by the present invention. A method for selective oxidation is provided, which gives rise to the formation of carboxylic and carbonyl groups at desired ratios in the cellulose. By using a phenoloxidase as the regenerative oxidant it is possible to avoid the environmentally harmful halide-containing materials commonly used as oxidants. The final electron acceptor is oxygen or hydrogen peroxide, which clearly diminishes the formation of by-products in the reaction system and which will make it easier to separate and purify the product. Furthermore, when oxidative enzymes, such as a phenoloxidase, are used as regenerative oxidants the oxidation can be carried out at mild reaction conditions: room temperature and about neutral pH.

Next the invention will be examined more closely with the aid of a detailed description and with reference to a number of working examples. The attached drawing depicts schematically the reactions of TEMPO in a oxidation system. Figure 1A shows the oxidation of TEMPO by chemical oxidants and Figure 1B gives the corresponding

presentation of the situation according to the present invention wherein the oxidation is achieved by enzymes.

As Figures 1A and 1B will show, the stable nitroxylradical (species 1) is oxidized to the oxoammonium ion (species 2), which oxidizes the alcohol group (RCH_2OH) e.g. to aldehyde (RCHO), while the oxoammonium ion at the same time is reduced to hydroxylamine (species 3).

The regenerative oxidant used in the case of Figure 1A is hypochlorite and in Figure 1B oxygen. In the first case, a catalytic amount of bromide is introduced into the reaction. The bromide will be oxidized to hypobromite which is a stronger oxidant than hypochlorite.

As mentioned above, different kinds of oxidative enzymes can be used. In particular, oxidative enzymes known to be capable of catalyzing oxidation of phenolic groups are used. These enzymes are often called phenoloxidases (E.C.1.10.3.2 benzenediol:oxygen oxidoreductase) and they catalyze the oxidation of o- and p-substituted phenolic hydroxyl and amino/amine groups in monomeric and polymeric aromatic compounds. The phenoloxidases include oxidases and peroxidases. "Oxidases" are enzymes which catalyze oxidative reaction using molecular oxygen as their substrate, whereas "peroxidases" enzymes which catalyze oxidative reactions using hydrogen peroxide as their substrate.

As specific examples of oxidases the following can be mentioned: laccases (EC 1.10.3.2), catechol oxidases (EC 1.10.3.1), tyrosinases and bilirubin oxidases (EC 1.3.3.5). Preferably, the enzymes used in the present invention are laccases. The laccases can be produced by white rot fungi, in particular by strains *Trametes* (formerly *Coriolus*) *versicolor* or *hirsuta* or *villosa*. Other known producers of laccase are the strains of the following genera: *Agaricus*, *Armillaria*, *Aspergillus*, *Botrytis*, *Fusarium*, *Lentinus*, *Monocillium*, *Neurospora*, *Phlebia*, *Polyporus*, *Podospora*, *Pycnoporus* and *Schizophyllum*.

The invention is not, however, limited to the indicated origins of the enzyme nor to the

isolation method, and the enzyme can also be obtained by other methods.

Thus, it is possible to produce the fenoloxidase enzyme by microorganisms, which have been mutated or genetically constructed to produce the desired enzyme, or by other production host strains, to which the gene encoding this enzyme has been transferred.

The amount of laccase used can be about 1 to 1000 nkat/g cellulose. The oxidation can be carried out in liquid phase, because TEMPO is water-soluble. The temperature is about 10 to 70 °C, preferably about 20 to 40 °C and the pH is 3 to 9. The amount of TEMPO is 0.01 to 50 weight-%, preferably about 0.1 to 20 weight-%, calculated from the amount of cellulose.

In practice, the reaction is carried out by dissolving a selected amount of TEMPO (in the form of the stable nitroxyl radical) into water: and suspending cellulose-containing substrate into the water phase to obtain a dry matter content of about 0.1 to 20 weight-%. A buffering agent can be added to the water to adjust the pH of the reaction medium to a value suitable for the laccase treatment (preferably 4 or higher). After the addition of laccase oxygen is introduced into the reaction mixture either as (pure) gas or as an airstream while agitating the mixture. The duration of the oxygen introduction will take about 10 min to 24 hours, depending on the amount of substrate to be oxidized. After the reaction, the oxidized cellulosic material is separated from the liquid by filtration, it is washed and dried, if required.

As mentioned above, peroxidases can also being used as oxidative enzymes for oxidizing TEMPO. In that case, the final electron acceptor is hydrogen peroxide.

As a result of the oxidation according to the present invention, an oxidized cellulose-containing material is obtained in which a part of the primary OH groups have been converted to carbonyl and carboxylic groups.

The method can be used for oxidizing fibres, in particular fibres of natural sources, such as cellulose from annual or perennial plants or trees. These fibres typically contain some

residues of the other components present in the source of origin, such as lignin and hemicellulose, in the case of cellulose fibres from tree pulp, and pectins in the case of cotton. As specific examples of oxidation substrates, fibres obtained from mechanical, chemical, chemimechanical or recycled pulps can be mentioned. These kinds of oxidized pulps can be used for preparing paper or boards having improved properties, in particular improved paper technical properties, flexibility, WRV and strength properties.

The method can also be employed for oxidizing cellulosic textile fibres, yarns and fabrics. These materials typically comprise cellulosic textile fibres selected from cotton, linen, hemp, ramie and viscose. Oxidation of the materials will increase the carboxylic group content of the fibres, yarns and fabrics and thus affect the properties thereof. Further TEMPO-based oxidation will provide fibres, yarns and fabric with modified properties selected from the group of handle, drapability, softness and water absorbency.

Finally, it should be noted that the use of traditional oxidants, such as hypochlorite and bromide for oxidization of cellulose fibres (defined above) via TEMPO is not disclosed in the prior art.

The following non-limiting examples illustrate the invention.

Example 1 (reference)

Chemical oxidation/hypochlorite and bromate and TEMPO mediated oxidation of ECF pine kraft pulp

As a reference, ECF pine kraft pulp was chemically oxidized by TEMPO together with hypochlorite and hypobromite (generated from sodium bromide) as described by (2).

5 g of ECF pine kraft pulp was suspended in 180 ml of water. 50 mg of TEMPO, 1.6 g NaBr and 60 ml of 8 % (w/v) hypochlorite solution (pH was adjusted to 10.8 by NaOH) were added to the suspension. The reaction mixture was stirred at room temperature for 5 hrs. pH was checked and adjusted to 10.6 by NaOH. After reaction the ECF pine kraft pulp was collected by filtration. It was washed by 5 times volume (5x250 ml) deionized

water and by 1 time volume 100 mM acetate buffer pH 5.0.

The carboxylic group content of the TEMPO-oxidized pulp and the reference pulp was analyzed by conductometric titration. The amount of carbonyl groups present in the pulp was estimated from the FTIR spectra at wavelength 1720-1620 cm^{-1} .

Table 1. Carboxylic and carbonyl group content of the reference ECF pine kraft pulp and the oxidized ECF pine kraft pulp

Pulp	COOH groups, mmol/kg	Carbonyl groups, relative units from FTIR
Ref	30	1
TEMPO oxidized pulp	900	5

According to the results, chemical oxidation by TEMPO and hypochlorite/-bromate generated new carboxylic groups in ECF pine kraft pulp. Also the amount of carbonyl groups was increased by oxidation. The amount of carboxylic and carbonyl groups in the pulp were increased 30 and 5 times, respectively, by the TEMPO oxidation.

Example 2

Enzymatical TEMPO-mediated oxidation/Laccase + TEMPO mediated oxidation of ECF-kraft pulp

Laccase + TEMPO mediated oxidation of ECF bleached pine kraft pulp was carried out at pH 5 with *Trametes* laccase (dosage 1000 nkat/g pulp). The reaction conditions were, consistency 1 %, pH 5, temperature room temperature. As a reference, the pulp was treated with laccase alone, TEMPO alone and without laccase or TEMPO. After the treatment the pulps were washed with distilled water. Carboxylic groups were measured by conducto-metric titration, carbonyl groups estimated by infrared spectroscopy and the carbohydrate composition was analyzed by HPLC after total enzymatic hydrolysis as described by (6). According to the HPLC analysis, the carbohydrates in the pulp were modified as compared to the reference. Also according to the FTIR analysis, the

modification was observed in the amount of carbonyl groups in the pulp.

TEMPO/laccase oxidation increased carbonyl groups in ECF pine kraft pulp about 25 %.

Example 3

5 Technical properties of the oxidized pulps

The technical properties, especially the water retention value WRV, of the laccase-
TEMPO-oxidized kraft pulp were measured before and after PFI-refining. The viscosity
of the pulp was also measured according to SCAN-method. According to the results the
10 properties were modified as a result of the increased amount of carboxylic and carbonyl
groups in the pulp.

Example 4

15 Cotton fibres were oxidized with laccase and TEMPO and the effect of the treatment on
the properties of the fibres were analyzed. Compared to the untreated fibres, the
properties of the laccase-TEMPO-treated cotton were modified.

REFERENCES

1. de Nooy, A.E.J., Besemer, A.C. and van Bakkum, H. (1996) Highly selective nitroxyl radical-mediated oxidation of primary alcohol groups in water-soluble glucans. Carbohydrate Research 269: 89-98.
2. Chang, P.S. and Robyt, J.F. (1996) Oxidation of primary alcohol groups of naturally occurring polysaccharides with 2,2,6,6-tetramethyl-1-piperidine oxoammonium ion. J.Carbohydrate Chemistry 15: 819-830.
3. Lindström, T. and Carlsson, G. (1982) The effect of chemical environment on fibre swelling. Svensk Papperstidning 85: R14-20.
4. Maurer, K. ja Drefahl, G. (1942) J. Am. Chem. Soc. 64: 121.
5. Semmelhack, M.F., Chou, D.A. and Cortes, J. (1983) J. Am. Chem. Soc. 105: 4492.
6. Tenkanen, M., Hausalo, T., Siika-aho, M., Buchert, J. and Viikari, L. (1995) Proc. 8th Int. Symp. Wood and Pulping Chemistry, Helsinki 6-9 June 1995, Vol III: 189.
7. Heinzkill, M. (1995) Isolierung und Charakterisierung von Laccase und Peroxidasen aus Basidiomyceten der Ordnung *Avaricales*. Ph.D thesis University of Kaiserslautern Germany, p. 178.
8. Krishna et al., 1992. Proc.Natl.Acad.Sci.USA. Vol 89. pp.5537-5541

Claims:

1. A method for preparing oxidized cellulose, which comprises bringing a cellulose-
containing material into contact with a reactant producing an oxoammonium ion in the
presence of an oxidizing agent, characterized in that an oxidative enzyme is used
as an oxidizing agent.

2. The method according to claim 1, wherein the reaction is carried out in a liquid
medium and the reaction product is separated from the medium after the reaction.

3. The method according to claim 1 or 2, which comprises using 2,2,6,6-
tetramethylpiperidine-1-oxyl (TEMPO) as the reactant producing an oxoammonium ion
and using an enzyme selected from laccase and peroxidase as the oxidizing agent.

4. The method according to claim 3, wherein oxygen or hydrogen peroxide is used as
electron acceptor.

5. The method according to any of claims 1 to 4, wherein the peroxidase is selected from
a laccase of the genera selected from *Trametes*, *Agaricus*, *Armillaria*, *Aspergillus*,
Botrytis, *Fusarium*, *Lentinus*, *Monocillium*, *Neurospora*, *Phlebia*, *Polyporus*, *Podospora*,
Pycnoporus and *Schizophyllum*.

6. A method of modifying cellulosic fibres, comprising the step of treating cellulose with
oxidized TEMPO.

7. The method according to claim 6, wherein TEMPO is chemically oxidized.

8. The method according to claim 6, wherein TEMPO is enzymatically oxidized using
laccase or a peroxidase.

9. The method according to any of the preceding claims, wherein pulp fibres are
oxidized.

10. The method according to claim 9, wherein pulp fibres selected from mechanical, chemical, chemimechanical and recycled pulps are oxidized.

11. The method according to claim 9 or 10, wherein the oxidized pulp can be used for preparing paper having improved properties selected from paper technical properties, flexibility, WRV and strength.

12. The method according to any of claims 1 to 9, wherein the cellulosic textile fibres, yarns or fabrics are oxidized.

13. The method according to claim 12, wherein cellulosic textile fibres selected from cotton, linen, hemp, ramie and viscose are oxidized.

14. The method according to claim 12 or 13, wherein the COOH content and the properties of the fibres, yarns or fabrics are modified.

15. The method according to claim 14, wherein the modified properties are selected from the group of handle, strength, drapability, softness and water absorbency.

1/1

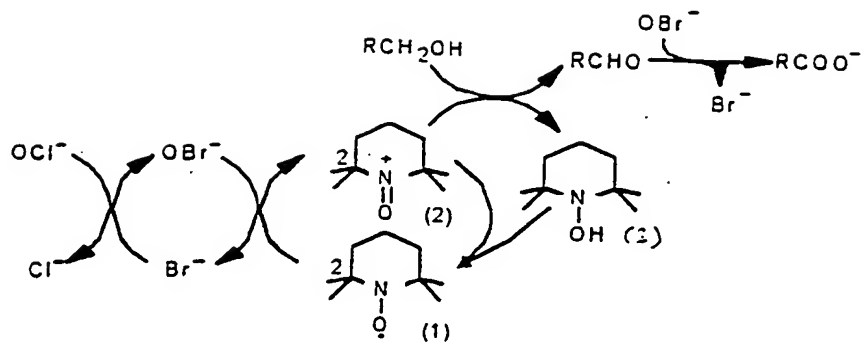


Fig. 1A

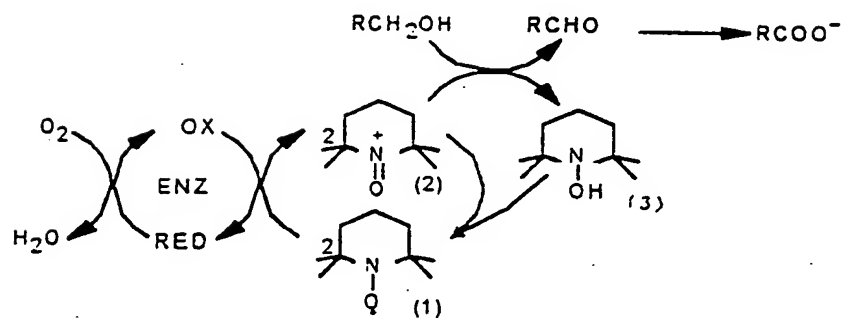


Fig. 1B

INTERNATIONAL SEARCH REPORT

International application No.

PCT/FI 98/00861

A. CLASSIFICATION OF SUBJECT MATTER

IPC6: C08B 15/04, C12S 3/00, D21C 9/10
According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

IPC6: C08B, C12S, D21C

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

SE,DK,FI,NO classes as above

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	WO 9429510 A1 (CALL, HANS-PETER), 22 December 1994 (22.12.94), page 5, paragraph 7 - page 6, paragraph 2; page 7, paragraph 4; page 10, paragraph 3 - page 11	1-2,5,9
Y	--	3-4,8,10-15
X	WO 9636621 A1 (COÖPERATIEVE VERKOOP- EN PRODUKTIEVERENING VAN AARDAPPELMEEL EN DERIVAT EN AVEBE B.A.), 21 November 1996 (21.11.96), page 7, line 3 - line 27, abstract, claims	6-7,9
Y	--	3-4,8,10-15

☒ Further documents are listed in the continuation of Box C.☒ See patent family annex.

* Special categories of cited documents:

- "A" document defining the general state of the art which is not considered to be of particular relevance
- "E" earlier document but published on or after the international filing date
- "L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)
- "O" document referring to an oral disclosure, use, exhibition or other means
- "P" document published prior to the international filing date but later than the priority date claimed

"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention

"X" document of particular relevance: the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone

"Y" document of particular relevance: the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art

"&" document member of the same patent family

Date of the actual completion of the international search

8 February 1999

Date of mailing of the international search report

09 -02- 1999

Name and mailing address of the ISA/

Swedish Patent Office
Box 5055, S-102 42 STOCKHOLM
Facsimile No. +46 8 666 02 86

Authorized officer

Jack Hedlund
Telephone No. +46 8 782 25 00

INTERNATIONAL SEARCH REPORT

International application No.

PCT/FI 98/00861

C (Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	WO 9612846 A1 (NOVO NORDISK A/S), 2 May 1996 (02.05.96), abstract, claims --	1-2
X	J. Carbohydrate Chemistry, Volume 15, No 7, 1996, Pahn S. Chang et al, "Oxidation of Primary Alcohol Groups of Naturally Occurring Polysaccharides with 2,2,6,6-Tetramethyl-1-Piperidine Oxoammonium Ion" page 819 - page 830 --	6-7,9
E	WO 9855684 A1 (CONSORTIUM FÜR ELEKTROCHEMISCHE INDUSTRIE GMBH), 10 December 1998 (10.12.98) --	1-15
E	DE 19723912 A1 (CONSORTIUM FÜR ELEKTROCHEMISCHE INDUSTRIE GMBH), 10 December 1998 (10.12.98) -- -----	1-15

INTERNATIONAL SEARCH REPORT
Information on patent family members

21/12/98

International application No.
PCT/FI 98/00861

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
WO 9429510 A1	22/12/94	AT 169699 T	15/08/98
		AU 680666 B	07/08/97
		AU 7124094 A	03/01/95
		AU 7739794 A	03/01/95
		BR 9406854 A	26/03/96
		CA 2165426 A	17/12/94
		CA 2182182 A	22/12/94
		CN 1127523 A	24/07/96
		CN 1129468 A	21/08/96
		CZ 9503325 A	15/05/96
		DE 59406698 D	00/00/00
		EP 0705327 A	10/04/96
		EP 0739433 A,B	30/10/96
		SE 0739433 T3	
		FI 956023 A	25/01/96
		FI 961157 A	13/03/96
		HU 74975 A	28/03/97
		HU 9503600 D	00/00/00
		JP 9500153 T	07/01/97
		NO 955111 A	07/02/96
		NO 961205 A	25/03/96
		NZ 268359 A	26/01/98
		NZ 273923 A	24/06/97
		SK 157995 A	09/07/97
		WO 9429425 A	22/12/94
WO 9636621 A1	21/11/96	AU 5704396 A	29/11/96
		NL 1000396 C	00/00/00
WO 9612846 A1	02/05/96	AU 3650295 A	15/05/96
		BR 9509394 A	30/09/97
		EP 0787230 A	06/08/97
		HU 77241 A	02/03/98
		JP 10507495 T	21/07/98
		PL 320062 A	01/09/97
WO 9855684 A1	10/12/98	DE 19723629 A	10/12/98
DE 19723912 A1	10/12/98	NONE	